

Methane Oxidation Behind Reflected Shock Waves—Ignition Delay Times Measured by Pressure and Flame Band Emission

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MEASURED BY PRESSURE AND FLAME BAND EMISSION

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SUMMARY

Ignition delay data were recorded for three methane-oxygen-argon mixtures ($\phi = 0.5, 1.0, 2.0$) for the temperature range 1500 to 1920 K. Quiet pressure traces enabled us to obtain delay times for the start of the experimental pressure rise. These times were in good agreement with those obtained from the flame band emission at 3700 Å. The data correlated well with the oxygen- and methane dependence of Lifshitz, but showed a much stronger temperature dependence ($\phi = 0.5 \Delta E = 51.9$, $\phi = 1.0 \Delta E = 58.8$, $\phi = 2.0 \Delta E = 58.7$ Kcal). The effect of probe location on the delay time measurement was studied. It appears that the probe located 83 mm from the reflecting surface measured delay times which may not be related to the initial temperature and pressure. It was estimated that for a probe located 7 mm from the reflecting surface, the measured delay time would be about 10 μ s too short, and it was suggested that delay times less than 100 μ s should not be used. The ignition period was defined as the time interval between start of the experimental pressure rise and 50 percent of the ignition pressure. This time interval was measured for three gas mixtures and found to be similar (40 to 60 μ sec) for $\phi = 1.0$ and 0.5 but much longer (100 to 120 μ s) for $\phi = 2.0$. It was suggested that the ignition period would be very useful to the kinetic modeler in judging the agreement between experimental and calculated delay times.

INTRODUCTION

Large computers have enabled us to assemble kinetic mechanisms for modeling the combustion of many fuels. These mechanisms may have as many as 150 reactions whose rates are treated as adjustable parameters and in some cases the only experimental parameter matched has been the ignition delay time obtained from shock tubes. Many studies have been conducted on the ignition of methane-oxygen gas mixtures in shock tubes (refs. 1 to 12). However, in some cases the data are in error due to probe location and in other cases the data are badly scattered due to poor measurements of the incident shock velocity or due to a very noisy pressure trace.

The delay time measured for a shock-heated hydrocarbon-oxygen mixture is known to be a function of initiation reactions, reactions of radicals and molecular oxygen with the fuel, and branching reactions. These branching reactions increase the radical concentrations to a level where ignition will occur. During ignition, there is rapid depletion of the primary fuel, very

high radical concentrations, and an exponential rise in temperature and pressure. Usually delay times are measured somewhere in this region by techniques which follow some physical process such as the change in pressure or the appearance of some emitting species. Although the time difference is small, one would like to determine the time of appearance of the signal as closely as possible. This time which is the start of the ignition process allows one to separate the fast ignition mechanism from the kinetics of the primary fuel.

This paper presents ignition delay data for the oxidation of methane measured with a quiet pressure transducer over the temperature range 1500 to 1920 K. The quiet pressure trace allowed the determination of the initial pressure rise. The delay times determined from this initial pressure rise are compared with the time of appearance of the expected flame band radiation at 3700 Å. In addition, the methane and CO₂ concentrations at the time of ignition will be measured. These parameters, which must be duplicated by any kinetic model, will be used to test the correctness of published kinetic mechanisms for methane-oxygen mixtures.

EXPERIMENTAL SECTION

The shock tube consisted of a single piece of square stainless steel tubing 5.7 m long, 64 mm on a side with 13 mm thick walls. The entire length of the tube was ground to constant inside dimension and then honed to a highly polished finish. Stations for shock wave detectors were located at 150 mm intervals in the downstream portion of the tube. Two 25 mm calcium fluoride windows were located 250 mm from the end of the tube. A quartz pressure transducer was located to provide an accurate indication of the time at which the shock wave arrived at the center of the windows. The assembled tube could be evacuated to a pressure of about 1 μ m and had a leak rate of less than 0.2 μ m per minute. A liquid nitrogen cold trap in the vacuum line guarded against the back-migration of pump oil into the shock tube.

The temperature and pressure behind the incident and reflected shock were calculated from the measured velocity of the incident shock wave with the shock program of Gordon and McBride (ref. 13). Since the reaction temperature must be calculated, it is very important to measure the initial temperature and the shock velocity as accurately as possible. The distance between probe locations was measured accurately to four significant figures. The shock tube wall temperature was measured to ± 0.5 C and it was assumed that the test mixture achieved this temperature rapidly. Thin film resistance gauges (1.3 cm in diameter) were used to detect the passage of the incident shock wave. The amplified output from these gauges were displayed on a digital oscilloscope (see fig. 1). Data points were recorded every 200 ns. One nice feature of this scope is that the scale can be magnified to allow each point to be viewed. This enabled the measurement of the incident shock velocity to better than ± 0.2 μ s (0.1 percent).

A 1.3 cm diameter nylon holder was designed to isolate the pressure transducer from the metal walls of the shock tube. This holder significantly reduced the noise level on the pressure trace. Remounting several of the other probes reduced the noise level even further. Finally it was found that the plug used to move the end wall of the shock tube to a location 7 mm from the center of the pressure transducer was a problem. The o-ring used to vacuum seal the plug to the flange at the end of the tube, acted like a spring when

the plug was struck by the shock wave. Apparently the plug moved back and forth and caused a pressure oscillation in the gas behind the reflected shock wave which could be seen by the pressure probe. The problem was eliminated by making a new plug without an o-ring.

All data were taken at a test gas pressure of 60 torr and a driver pressure of 115 psia. Soft aluminum diaphragms separated the high pressure driver gas from the test gas. These diaphragms were pressurized and pierced by a gas activated piston. The shock strength was varied by changing the molar mass of the driver gas with the addition of small amounts of argon to the helium driver gas. Figure 2 shows the variation of shock velocity with the reciprocal of the molar mass of the driver gas. The constant pressure ratio across the diaphragm insured that the opening process for the diaphragm was about the same for all tests.

Gas mixtures were prepared by the method of partial pressures in 34.4 liter stainless steel tanks. The gases used to prepare the mixtures had stated purities of 99.99 percent methane, 99.98 percent oxygen, and 99.998 percent argon. The partial pressure of methane and oxygen could be determined to better than 0.3 torr and the total pressure of the tank to better than 0.2 psia. All samples were prepared to a total pressure of 60 psia.

The mixture strength was selected to give similar temperature rises at ignition for all equivalence ratios (see table I). This procedure insured that the behavior of the ignition process would be similar unless the kinetics were different. Burcat (ref. 14) presented traces showing the pressure and heat transfer histories during the ignition of propane-oxygen-argon gas mixtures. Although the shock temperatures were the same for all three mixtures, ($\phi = 1.0$, 1.6 percent C_3H_8 -8 percent O_2 ; $\phi = 1.0$, 3.85 percent C_3H_8 -19.2 percent O_2 ; and $\phi = 0.5$, 0.8 percent C_3H_8 -8 percent O_2), the pressure and heat transfer history were greatly altered as the temperature rise available at ignition was decreased. The degree of difficulty in selecting the correct delay time increased as the temperature rise decreased. Our pressure traces for the three mixtures (fig. 3) show about the same character at ignition and demonstrates the value of having the same temperature rise.

Radiation at 3700 Å was monitored for each experiment and displayed on the oscilloscope with the pressure history. The radiation was detected by a photomultiplier tube whose field of view was restricted by two slits 0.75 and 1.5 mm wide, located 10 and 23 cm from the center of the shock tube. This arrangement enabled us to view a 3 mm slice of the hot gas in the center of the shock tube at the same location as the pressure transducer. An interference filter centered at 3696.5 Å with a half band width of 115 Å was used to isolate the 3700 Å radiation. The filter transmitted 51 percent of the incident radiation. The high voltage power supply for the photomultiplier tube was adjusted so that the peak emission for $\phi = 0.5$ could be detected. It was thought that this arrangement would allow us to observe the trends indicated by the kinetic model.

RESULTS AND DISCUSSION

Ignition Delay Times and Probe Location

Frenklach (ref. 15) measured ignition delay times at two locations in a shock tube and concluded that the location of the probe must be taken into consideration when selecting delay time data to be modeled by a kinetic mechanism. Since optical access was necessary to monitor the infrared and ultraviolet radiation behind the reflected shock wave, it is important to know the error involved in measuring the delay time 7 mm from the reflecting surface. Two pressure transducers were located 7 and 83 mm from the reflecting surface. These allowed the simultaneous measurement of the delay time at two locations in the same experiment (see fig. 4). An ethane-oxygen-argon mixture (1.27, 5.05, and 93.68 percent) was used for this series of tests. For these experiments, the definition of the delay time was the time at which the ignition pressure exceeded the reflected shock pressure (P_5) by 10 percent. This eliminated the guess work usually involved in determining the point at which the pressure departed from the flat portion of the trace.

Figure 5 is a plot of the delay times for the two locations as a function of $1/T$. The 7 mm position was fitted by a straight line while the 83 mm position required a curve fit. The delay time measured for the 83 mm position was always shorter than that for the 7 mm position. This behavior may be explained in part with the time-distance plot of the trajectory of the incident and reflected shock waves near the end of the shock tube shown in figure 6. Although the incident shock wave preheated the gas, no reaction takes place until the shock reflects from the end wall. The time at which reflected shock heating occurs at a given location along the tube is a function of its distance from the reflecting surface and the reflected shock velocity. In this case, the gas near the end wall has been heated 15 and 200 μ s longer than the gas at the two probe positions, respectively. Therefore, ignition will first occur near the end wall. The pressure rise due to ignition causes a disturbance to propagate down the tube. The minimum propagation velocity of the disturbance is the sonic speed in the shocked gas. However, the schlieren photographs behind the reflected shock wave presented in Vermeer (ref. 16) clearly shows that the disturbance propagates much faster than the reflected shock wave. The data in figure 5 was used to calculate the propagation velocity between the two probes. This velocity had an average value of 1660 m/s, which is a Mach number of about 2.5. This velocity is about four times that of the reflected shock wave. Therefore, the delay times measured at the 7 mm position are estimated to be too small by about 10 μ s. This error would not be important unless the measured delay times were near 100 μ s. No corrections have been made to the present data but delay times less than 100 μ s are not considered reliable.

Another disturbing feature of the pressure traces was the amplitude of the ignition pressure. Unless something has changed, one would expect the ignition pressure to be the same at all locations in the tube. However, the ignition pressure for probe 2 (83 mm location) is much larger than that at probe 1 (7 mm location) (see fig. 4). The ratio of the ignition pressure to the reflected shock pressure (P_5) for the two probe positions are plotted versus the delay time at probe 1 in figure 7. Note that this ratio is nearly constant at probe 1 but increases with decreasing delay times at probe 2. This suggests that the gas properties at ignition are not the same at the two locations

Ignition Delay Times

Ignition delay times were measured behind reflected shock waves for the mixtures shown in table I. The pressure history and the carbon monoxide flame band emission at 3700 Å were used to determine the onset of ignition. Figure 3 shows a typical pressure and emission record for the three gas mixtures. The ignition pressure shows a reasonable exponential rise and the time at which the pressure started to increase could be selected with reasonable confidence ($\pm 15 \mu\text{s}$). However, the start of the exponential pressure rise for the rich mixture ($\phi = 2.0$) could not be determined with the same confidence level. This was because a small but steady rise in the pressure occurred long before ignition and interfered with the initial pressure rise. The flame band radiation in the lower trace has a sharp spike and the point at which the signal first appeared could be selected within $\pm 10 \mu\text{s}$.

The delay times measured by both pressure and flame band emission are recorded in table II. These delay times may be correlated by an empirical relation of the form:

$$t = A \exp(B/RT) [\text{CH}_4]^a [\text{O}_2]^b [\text{Ar}]^c \quad (1)$$

Lifshitz (ref. 8) and Tsuboi (ref. 12) both found an overall pressure dependence of -0.7 for $a + b + c$. Plots of $\tau p^{0.7}$ versus $1/T$ for each mixture are shown in figure 8 and a least square fit to the data yielded the following equations:

$$\phi = 0.5 \quad \tau p^{0.7} = 9.59 \times 10^{-5} \exp(51.93 \times 10^3/RT) \mu\text{sec-atm}^{0.7} \quad (2)$$

$$\phi = 1.0 \quad \tau p^{0.7} = 2.85 \times 10^{-5} \exp(58.83 \times 10^3/RT) \mu\text{sec-atm}^{0.7} \quad (3)$$

$$\phi = 2.0 \quad \tau p^{0.7} = 3.65 \times 10^{-5} \exp(58.74 \times 10^3/RT) \mu\text{sec-atm}^{0.7} \quad (4)$$

A correlation of all of the data in the form used by Lifshitz, $\tau [\text{CH}_4]^{0.33} [\text{O}_2]^{1.03}$ is shown in figure 9. The activation energies in equations (2) to (4) for the present data are larger than those found by Lifshitz and appear to depend upon the oxygen concentration.

The mixtures for $\phi = 1.0$ and 2.0 have 4 percent oxygen and the same activation energy, while the mixture for $\phi = 0.5$ with 8 percent oxygen has a measurably lower activation energy. The same behavior has been reported by Tsuboi.

Ignition Period

The measurement of the ignition period should be useful to the modelers as a tool for selecting the parameter to determine when the calculated delay time fits the experimental one. The ignition period was arbitrarily defined to be the time interval between when ignition occurred (start of pressure rise) and when the experimental ignition pressure reached 50 percent of its peak value. Experimentally the first pressure peak was selected because it appears to indicate the end of the exponential rise in the pressure.

Ignition periods were measured for the three gas mixtures and are plotted versus ignition times in figure 10. Although the data are badly scattered some conclusions can be obtained from them. In general, the ignition period is small compared to the delay time. For equivalence ratios of 1.0 and 0.5 the periods are about the same and have values of 40 μm at a 200 μs delay time and 60 μs at 1500 μs . However, for the rich mixture ($\phi = 2.0$), the ignition period is much longer, ranging from 100 to 120 μs for the same range of delay times.

An example of the value of this measurement can be seen in figure 11, which shows pressure profiles calculated by the kinetic mechanism proposed by Westbrook (ref. 17). The calculations were made with the packaged code LSODE, as discussed in references 18 to 20. The temperature and pressure for three of the $\phi = 1.0$ experiments were used as input for the program. The times for the initial pressure rise measured in each experiment are indicated on the figures. The calculation shows a rise in pressure which corresponds to these times. Although this looks like a good match between the calculated and experimental delay times, the ignition periods are not the same. The calculations give ignition periods of 160 to 270 μsec , while the experiments show periods of 40 to 60 μs .

Radiation at 3700 Å

The ignition delay time was measured also with UV radiation at 3700 Å. At present it is not clear whether this radiation is from the blue continuum of the carbon monoxide flame bands or from some hydrocarbon species. Jachimowski (ref. 1) first observed a spike setting on the leading edge of the flame band radiation while studying methane oxidation behind an incident shock wave. He attributed this to some kind of hydrocarbon emission and presented a convincing argument to justify this conclusion. These experiments were done at 2558 K. Heffington, et al. (ref. 2) suggested that it is likely that the observed intensity profiles for CO-O recombination indicate very rapid build-up and decay of oxygen atoms during the "spike" region identified by Jachimowski. Their temperature range was 1930 to 2850 K. Bowmans' (ref. 3) flame band emission data suggest that there is an underlying emission which cannot be attributed to the chemiluminescent reaction of O-atoms and CO. The intensity of this underlying emission increases with increasing temperature (1875 to 2240 K). He did find that the peak radiation increased when CO was added to the gas mixture, but the change in this radiation was not proportional to the amount of CO added.

Calculations performed with the kinetic model of Westbrook (ref. 17) for the oxidation of methane produced some interesting results. At ignition, the oxygen atom concentration increased by almost two orders of magnitude. The peak CO by O concentrations were found to decrease with increasing equivalence ratio $\phi = 0.5 > \phi = 1.0 > \phi = 2.0$. The addition of 0.5 and 1.0 percent CO to the gas mixture showed that the peak CO by O concentrations were not proportional to the amount of CO added as Bowman had indicated. Thus the calculations at 1800 K suggest that the "spike" in the radiation at 3700 Å may be explained on the basis of a rapid change in the O-atom concentration as well as by hydrocarbon emission.

For each experiment, the time of appearance of the radiation and the time when the radiation peaked were recorded. In addition, the peak height was

measured. The time at which the radiation appeared was found to be in excellent agreement with the time selected for the initial pressure rise ($\pm 10 \mu\text{s}$ in most cases). It was much easier to determine the time when the radiation first appeared than when the initial rise in pressure occurred.

The peak signals for the radiation at 3700 Å are plotted against the reflected shock temperature in figure 12. For the three mixtures studied, the signal strength was $\phi = 0.5 > \phi = 1.0 > \phi = 2.0$. The order is the same as that calculated by the kinetic model. The concentration of methane was the same for $\phi = 0.5$ and 1.0 (2 percent), but was twice as large for $\phi = 2.0$ (4 percent) which produced the smallest signal. If this emission were from some hydrocarbon species as suggested, one would expect the signal to be strongest for the fuel rich mixture. Data taken with added CO may shed more light on what is really being viewed at 3700 Å.

Delay times determined from the emission record are given in table II and the least squares equation for $\tau_p^{0.7}$ are:

$$\phi = 0.5 \quad \tau_p^{0.7} = 1.78 \times 10^{-4} \exp(50.00 \times 10^3 / RT) \quad (5)$$

$$\phi = 1.0 \quad \tau_p^{0.7} = 2.94 \times 10^{-5} \exp(58.73 \times 10^3 / RT) \quad (6)$$

$$\phi = 2.0 \quad \tau_p^{0.7} = 2.62 \times 10^{-5} \exp(59.85 \times 10^3 / RT) \quad (7)$$

The time interval between the appearance of the emission and when it peaked showed an interesting similarity with the ignition period data taken from the pressure records. Figure 13 shows this time interval versus the measured delay time. Note that the time interval was short for $\phi = 1.0$ and 0.5 and was long for $\phi = 2.0$ as observed by the pressure measurements. Although the times measured by the two methods are different, the difference is small. And in cases where the pressure could not be used for measurement of the ignition period, the emission may be of equal value.

SUMMARY OF RESULTS

Ignition delay data were recorded for three methane-oxygen-argon mixtures ($\phi = 0.5, 1.0, 2.0$) for the temperature range 1500 to 1920 K. Quiet pressure transducers enabled us to obtain delay times for the start of the experimental pressure rise. These times were in good agreement with those obtained from the flame band emission at 3700 Å. The data correlated well with the oxygen and methane dependence of Lifshitz, but showed a much stronger temperature dependence ($\phi = 0.5 \Delta E = 51.9$, $\phi = 1.0 \Delta E = 58.8$, $\phi = 2.0 \Delta E = 58.7$ Kcal).

The effect of probe location on the delay time measurement was studied. It appears that the probe located 83 mm from the reflecting surface measured delay times which may not be related to the initial temperature and pressure. It was estimated that for a probe located 7 mm from the reflecting surface, the measured delay time would be about 10 μs too short, and it was suggested that delay times less than 100 μs should not be used.

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TABLE I. - COMPOSITION OF GAS
MIXTURES AND TEMPERATURE RISE
DUE TO IGNITION

Percent				
ϕ	CH ₄	O ₂	Ar	Temperature rise due to ignition, K
0.50	2	8	90	894
1	2	4	94	882
2	4	4	92	729

TABLE II. - IGNITION DELAY TIMES MEASURED BY PRESSURE
AND FLAME BAND EMISSION

$\phi = 0.5$ 2% CH₄ - 8% O₂ - 90% Argon

Temperature, K	(1/T)×10 ⁴ , K ⁻¹	Pressure, atm	Delay times (μsec)	
			Pressure	Emission
1778	5.624	3.464	99	110
1763	5.672	3.418	102	110
1752	5.708	3.371	112	125
1730	5.780	3.318	159	167
1695	5.900	3.199	201	208
1687	5.928	3.191	208	209
1657	6.035	3.072	323	322
1620	6.173	2.979	508	512
1610	6.211	2.950	533	542
1605	6.231	2.918	594	597
1601	6.246	2.922	672	672
1579	6.333	2.857	663	658
1576	6.345	2.835	742	738
1555	6.431	2.773	850	858
1554	6.435	2.786	958	964
1531	6.532	2.704	1144	1145
1499	6.671	2.613	1655	1649

$\phi = 1.0$ 2% CH₄ - 4% O₂ - 94% Argon

1915	5.222	3.680	57	59
1866	5.359	3.536	84	78
1802	5.549	3.354	171	166
1780	5.618	3.279	201	219
1775	5.638	3.278	185	192
1746	5.727	3.183	295	295
1732	5.774	3.147	383	383
1725	5.797	3.122	397	396
1710	5.848	3.082	427	414
1707	5.858	3.077	531	559
1689	5.921	3.023	525	522
1689	5.921	3.032	589	589
1655	6.042	2.932	794	775
1645	6.079	2.900	867	861
1635	6.116	2.876	967	973
1629	6.139	2.855	1072	1075
1615	6.192	2.822	1163	1144
1593	6.278	2.761	1448	1471

TABLE II. - (concluded)

 $\varphi = 2.0$ 4% CH₄ - 4% O₂ - 92% Argon

Temperature, K	(1/T)x10 ⁴ , K ⁻¹	Pressure, atm	Delay times (μsec)	
			Pressure	Emission
1922	5.203	4.012	67	62
1856	5.388	3.797	116	110
1789	5.590	3.583	198	201
1770	5.650	3.524	249	271
1763	5.672	3.485	318	304
1730	5.780	3.381	369	368
1715	5.831	3.351	509	501
1712	5.841	3.326	489	486
1691	5.914	3.260	690	682
1681	5.949	3.228	765	767
1677	5.963	3.217	795	797
1650	6.061	3.134	1102	1096
1627	6.146	3.063	1214	1221
1621	6.169	3.043	1319	1321
1602	6.242	2.984	1534	1557

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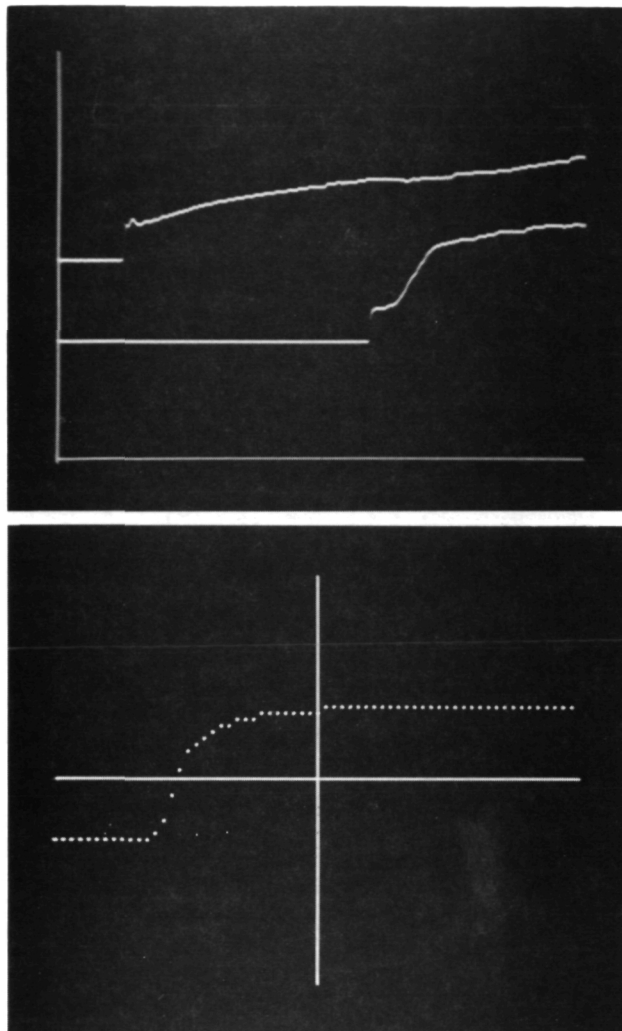


Figure 1. - Shock velocity measurement. Output from thin-film probe amplifier fed to digital oscilloscope. Time per point is 200 ns. Lower trace shows expansion of scale which is helpful in determining exact time shock wave passed probe position.

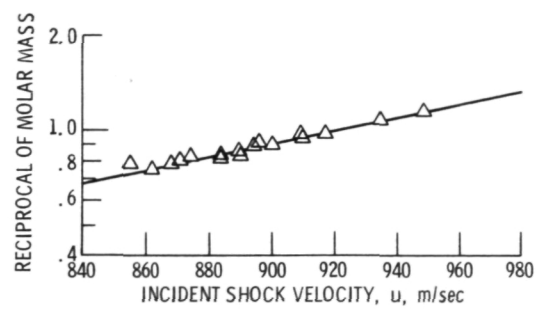


Figure 2. - Shock velocity as a function of the molar mass of the driver gas for a constant pressure ratio across the diaphragm.

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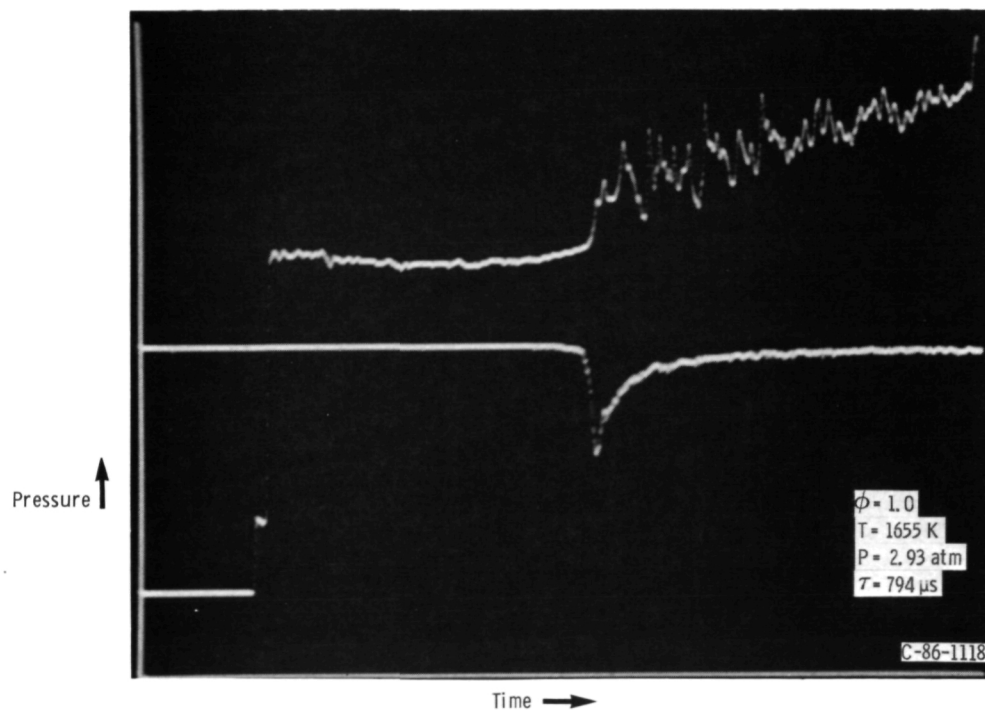
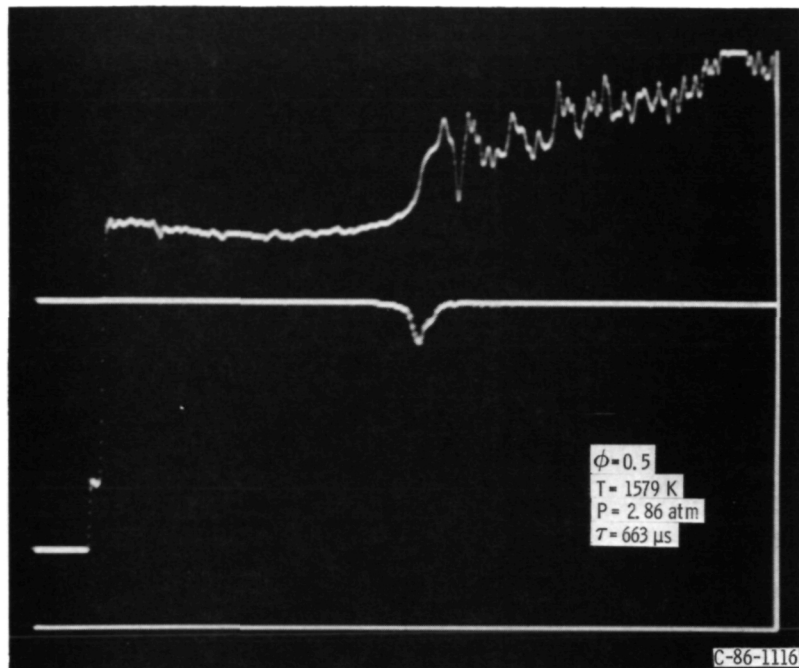


Figure 3. - Pressure and emission record for each mixture.

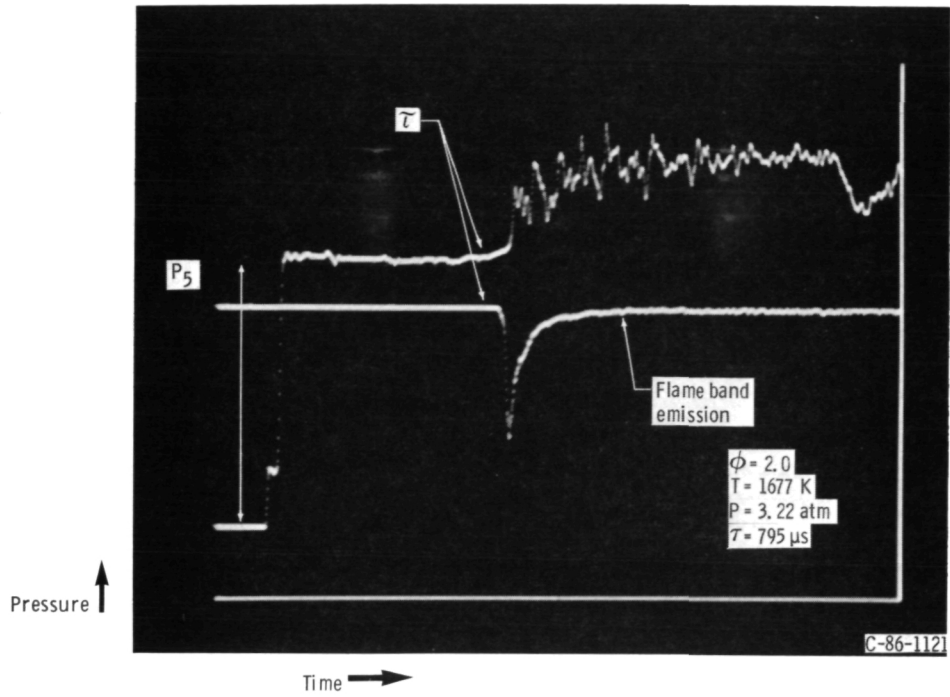


Figure 3. - Concluded.

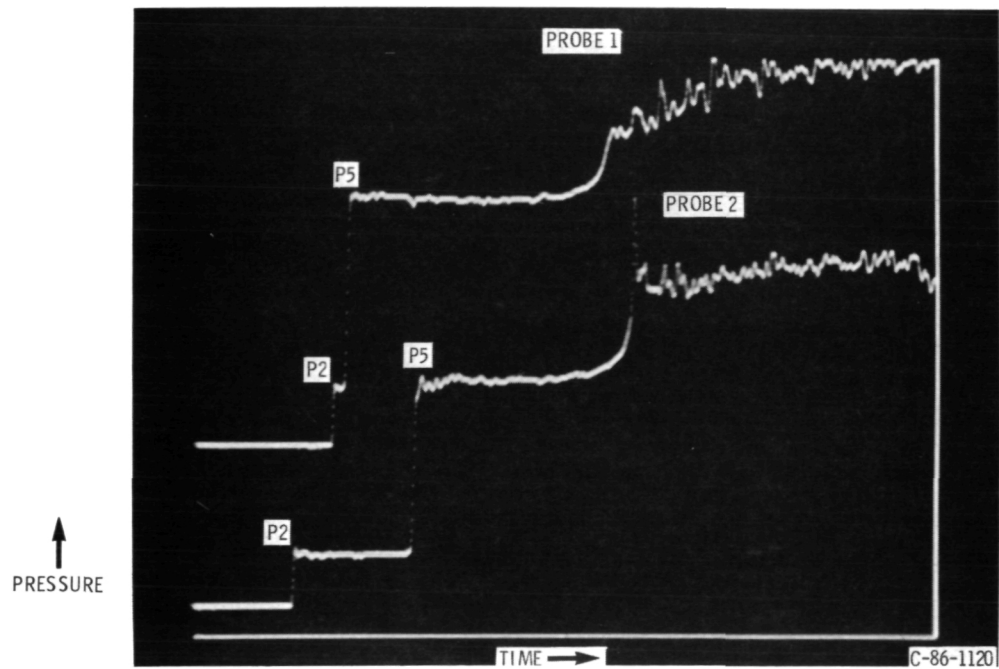


Figure 4. - Delay times measured at two locations in the shock tube. Probe 1 is 7 mm from the reflecting surface and probe 2 is 83 mm. P2 is the incident shock pressure and P5 is the reflected shock pressure. Measured delay times were 712 and 574 μs .

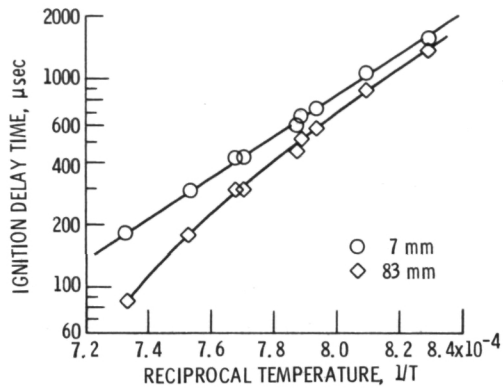


Figure 5. - Ignition delay times for a 1.27-percent C_2H_6 , 5.05-percent O_2 , 93.68-percent Ar ($\phi = 0.88$) mixture, as recorded at two different locations along the shock tube.

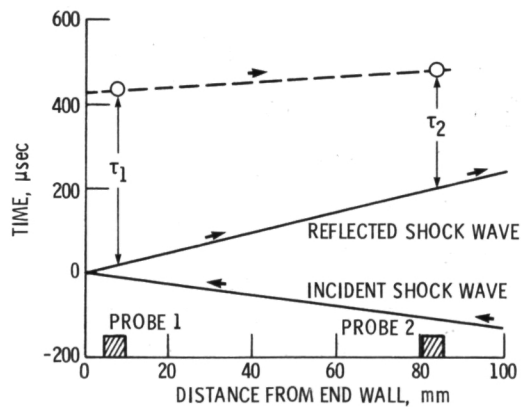


Figure 6. - Time-distance diagram of incident and reflected shock trajectory and delay times measured at two locations. Propagation of ignition wave shown by dashed line.

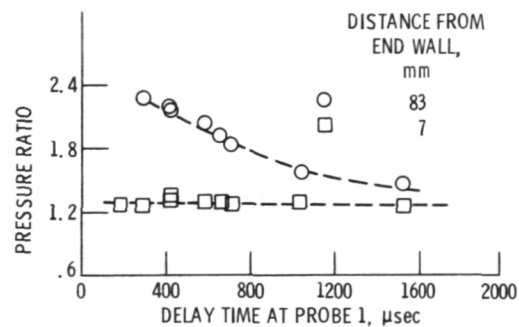


Figure 7. - Ratio of ignition pressure to reflected shock pressure, demonstrating enhanced ignition at the second probe position, particularly for shorter delay times.

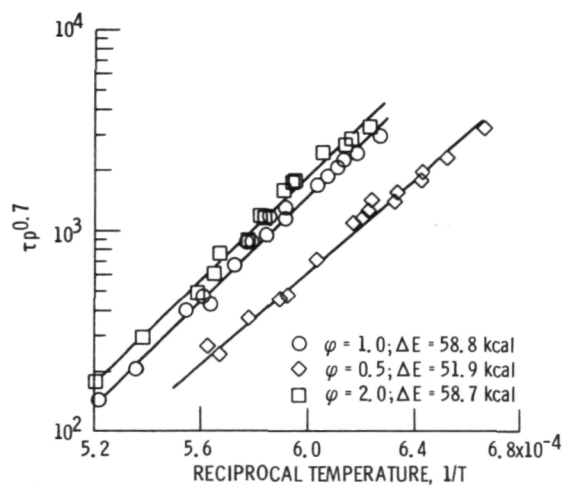


Figure 8. - $\tau p^{0.7}$ plotted versus $1/T$ for all three CH_4 mixtures, $\phi = 0.5$, $\phi = 1.0$, and $\phi = 2.0$.

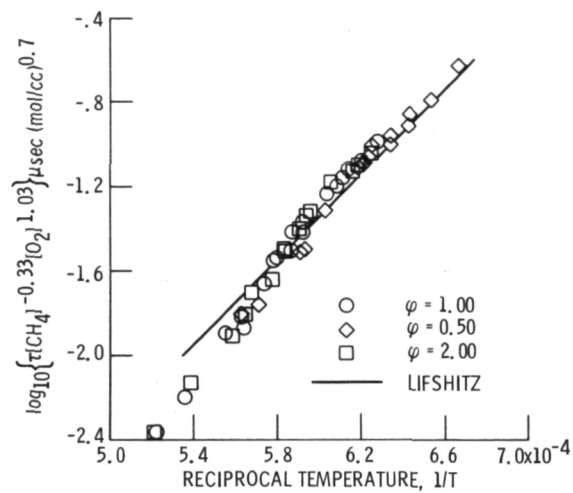


Figure 9. - All CH_4 data ($\phi = 0.5$, $\phi = 1.0$, $\phi = 2.0$) plotted as proposed by Lifshitz. Agreement with the literature is seen to be quite good.

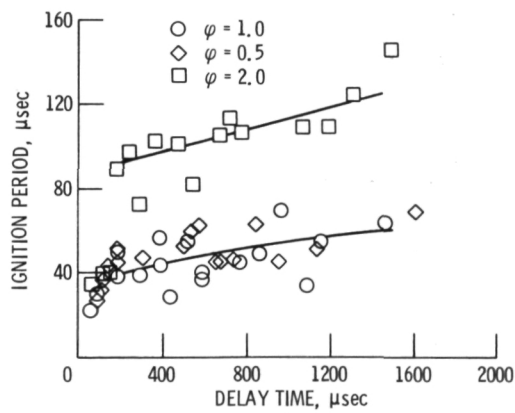


Figure 10. - Length of ignition period plotted versus delay time for all three CH_4 mixtures. This shows the increased ignition period for the $\phi = 2.0$ mixture.

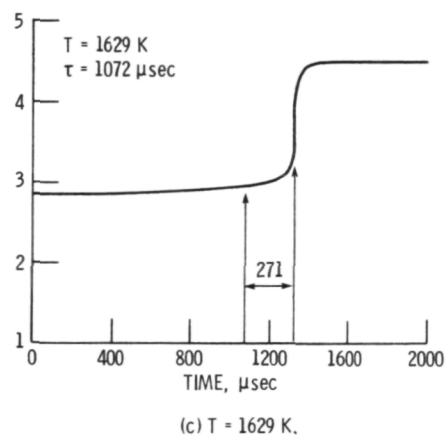
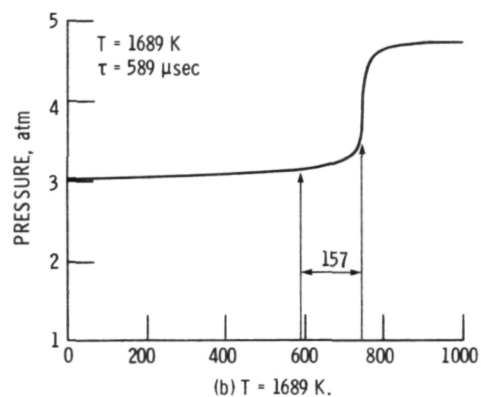
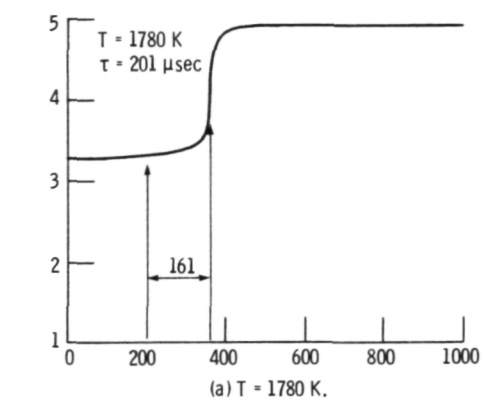


Figure 11. - Calculated pressure profiles for the $\phi = 1.0$ mixture at (a) $T = 1780\text{ K}$, (b) 1689 K , and (c) 1629 K . Calculations were made using the chemical kinetic mechanism proposed by Westbrook.

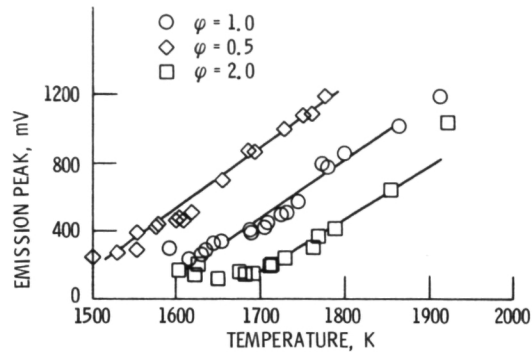


Figure 12. - Peak flame band emission at 3700 Å plotted against reflected shock temperature for all three methane mixtures ($\phi = 0.5$, $\phi = 1.0$, $\phi = 2.0$).

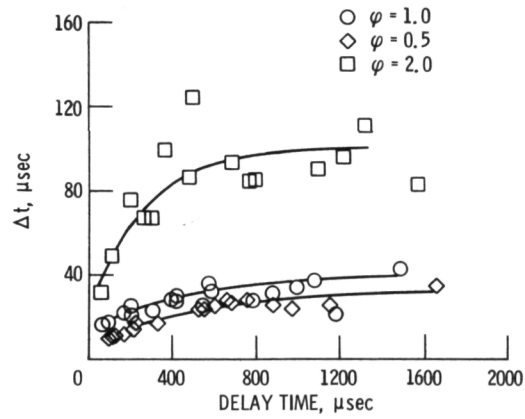


Figure 13. - Time interval between onset of emission and peak emission plotted versus delay time for all three methane mixtures. This also shows a larger time interval for the $\phi = 2.0$ mixture.

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16. Abstract Ignition delay data were recorded for three methane-oxygen-argon mixtures ($\phi = 0.5, 1.0, 2.0$) for the temperature range 1500 to 1920 K. Quiet pressure trances enabled us to obtain delay times for the start of the experimental pressure rise. These times were in good agreement with those obtained from the flame band emission at 3700 Å. The data correlated well with the oxygen and methane dependence of Lifshitz, but showed a much stronger temperature dependence ($\phi = 0.5 \Delta E = 51.9, \phi = 1.0 \Delta E = 58.8, \phi = 2.0 \Delta E = 58.7$ Kcal). The effect of probe location on the delay time measurement was studied. It appears that the probe located 83 mm from the reflecting surface measured delay times which may not be related to the initial temperature and pressure. It was estimated that for a probe located 7 mm from the reflecting surface, the measured delay time would be about 10 μs too short, and it was suggested that delay times less than 100 μs should not be used. The ignition period was defined as the time interval between start of the experimental pressure rise and 50 percent of the ignition pressure. This time interval was measured for three gas mixtures and found to be similar (40 to 60 μsec) for $\phi = 1.0$ and 0.5 but much longer (100 to 120 μs) for $\phi = 2.0$. It was suggested that the ignition period would be very useful to the kinetic modeler in judging the agreement between experimental and calculated delay times.					
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